MAGNETIC SEMICONDUCTORS

Engineering ferromagnetism

Semiconductors that exhibit room-temperature ferromagnetism are central to the development of semiconductor spintronics. Manganese-doped chalcopyrites are a promising class of such materials, but their success will depend on our ability to understand and optimize their behaviour. First-principles materials design could provide a way to achieve these goals.

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The goal of the emerging field of spintronics[1] is to find ways to manipulate and use electronic spin to the same degree that electronic charge is used in silicon-based electronics. Achieving this goal could lead to significant improvements in the performance of digital information processing and storage devices. To do so will require the development of new semiconducting materials that show ferromagnetism upon transition-metal doping — known as dilute magnetic semiconductors (DMS) — and that maintain their ferromagnetic behaviour at room temperature. Alongside the concerted experimental search to find such materials, first-principles calculations that self-consistently incorporate both charge and spin within an approach based on density functional theory are increasingly being used to provide important clues to where the experimental effort might best be directed. On page 410 of this issue, Steven Erwin and Igor Žutić[2] report the results of such theoretical calculations, focusing on one promising class of materials known as the Mn-doped chalcopyrites.

The archetypal DMS, Mn-doped gallium arsenide[3], has been the subject of intense research in recent years and has the benefit of being compatible with GaAs technology. However, the low solubility of Mn, and the occurrence of phase segregation at Mn concentrations beyond a few per cent, have severely limited the outlook for achieving room-temperature ferromagnetism in this material. In comparison, the potential of the chalcopyrites — a versatile class of semiconductors, long known to materials scientists — has only recently become apparent with the discovery of room-temperature ferromagnetism in heavily Mn-doped $CdGeP_2$ (ref. 4), spawning a whole new class of potential DMS[5,6].

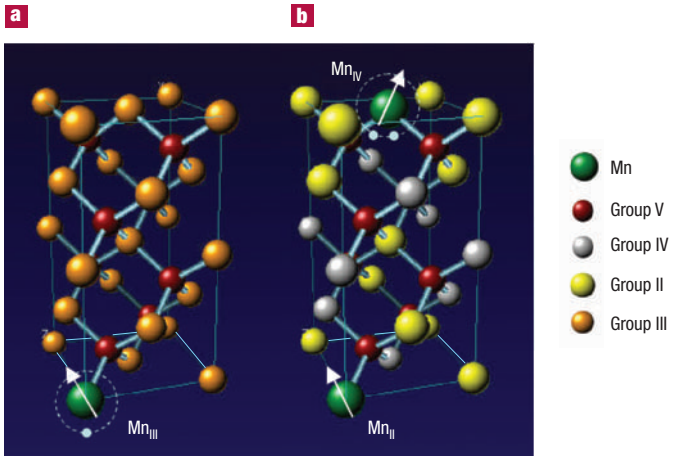

Figure 1 The widely accepted origin of ferromagnetism in dilute magnetic semiconductors. **a**, In a Mn-doped III-V binary semiconductor such as (Ga,Mn)As, each Mn atom substituted onto a group-III site (Mn_{III}) contributes a single hole (small azure circle, here represented as localized around the Mn atom) and a local magnetic moment (white arrow). **b**, In a Mn-doped II-IV-V_2 chalcopyrite, Mn atoms can be incorporated substitutionally in two ways; isovalently at the electrically inactive group-II site (basal plane, Mn_{II}), or heterovalently at the group-IV site (uppermost plane, Mn_{IV}). The Mn atom contributes a local magnetic moment in both iso- and heterovalent substitution. But the latter also enables the Mn atom to contribute up to two holes, leading to qualitatively different magnetic behaviour.

Pure chalcopyrites are ternary compounds with the chemical formula II-IV-V_2, where II, IV and V represent respectively elements from groups II, IV and V of the periodic table. Their structures can be derived

from III-V zinc-blende semiconductors[7], with the group-III atom in the binary compound being alternately replaced by elements from groups II and IV. In its un-doped state, the electronic contributions of a chalcopyrite's group-II and group-IV atoms average out to contribute no net carriers to the lattice. When substitutionally doped with Mn, however, the electrical activity of the Mn atom will be determined by which of these cations it replaces. All Mn atoms within the lattice contribute magnetic moments, but when substituted on the group-II site, each Mn atom contributes no free carriers to the lattice, whereas on the group-IV site, each contributes up to two holes. This contrasts significantly with the situation for III-V-based DMS — such as (Ga,Mn)As — in which the heterovalent substitution of Mn^{2+} at the group-III site always contributes one carrier and a local magnetic moment to the system (Fig. 1).

This behaviour underlines the inherent versatility of the chalcopyrites, and makes them ideal potential candidates for ferromagnetic engineering, though their controlled synthesis has not yet been achieved. Experimentally, chalcopyrites can readily contain both cation vacancies and substitutional defects (the location of a group-II ion on a group-IV site), both of which contribute free holes to the lattice. According to Dietl[8], ferromagnetism in DMS is a carrier-mediated mechanism and, as such, favoured by holes. The presence of defects was invoked to explain the observation of room-temperature ferromagnetism in $MnCdGeP_2$ (ref. 9). But can this be generalized to the whole class of chalcopyrites, and, more importantly, can their magnetic behaviour be optimized for spintronic applications?

Despite the extensive research devoted to DMS, remarkably little is known about how the host-specific properties of a DMS, such as bandgap or lattice constant, affect its ferromagnetic behaviour. To answer such questions, Erwin and Žutić[2] conduct a systematic first-principles study of 64 different types of Mn-doped II-IV-V_2 chalcopyrite, focusing on the correlation between magnetism and the structural and electronic properties of the host semiconductor[2]. Their analysis leads to a number of important conclusions.

First, it suggests that the two most common models proposed to explain ferromagnetism in DMS — namely, the Zener[8] and double-exchange[10] models — are neither flexible nor accurate enough to describe the properties of real materials. Second, contrary to conventional wisdom, the observed preference for Mn substitution on the group-II site is not common to all chalcopyrites, but depends on growth conditions and on the nature of the host lattice. Last, and perhaps most significantly, the authors identify valuable trends in the magnetic properties of the chalcopyrites that could be used by researchers to focus their attention on a restricted set of materials that exhibit all the characteristics considered desirable for spintronic applications. Such characteristics include thermodynamic stability, lattice-matching with common semiconductors, favourable Mn-doping, ferromagnetism and half-metallicity (the peculiar phenomenon displayed by most DMS, in which a material's metallic versus semiconducting character depends on the spin of the carriers, thereby leading to 100% spin-polarized carriers at the Fermi level).

So what does the future hold for engineering the ferromagnetic properties of prospective spintronic materials? On the theory side, the work of Erwin and Žutić should stimulate similar projects focused on other classes of DMS — such as transition-metal-doped oxides, as well as binary or ternary compounds — whose behaviour is still poorly understood, especially in terms of optimizing their properties. More theoretical work will be needed to understand the nature of ferromagnetism in chalcopyrites, in particular with respect to the long-range versus short-range character of the magnetic interactions or the effects of crystalline defects. On the experimental side, this work will help to direct researchers to refine the synthesis of selected promising chalcopyrites (before and after Mn-doping), to resolve outstanding growth issues (such as clustering and phase segregation) and to improve the quality of materials used for making devices. And at the interface between theory and experiment, it will be interesting to see how well the authors' first-principles approach — given the acknowledged weaknesses of density functional theory in correctly describing electron correlations and finite-temperature effects — predicts the properties of yet-to-be-synthesized materials, particularly given the influence that could be exerted by defects, complexes and competing phases. If the authors are as successful in predicting the properties of future materials as they have been in calculating the properties of known Mn-doped chalcopyrites[4], we could indeed be entering the realm of ferromagnetically-engineered DMS materials.

References

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